Nanocomposite Silica Thin Films

Solution of EtOH, H₂O, TEOS, HCl and surfactant[1]

Surfactant organizes into micelles as EtOH evaporates

Hexagonally packed micelles give a meso-structure to film

Sol-gel Chemistry

UV-Light 187-254 nm

UV light, in conjunction with the ensuing production of activated oxygen and ozone, removes the surfactant phase and strengthens the silicate phase by fostering the condensation of unreacted silanols. This creates a mesoporous film with pores where the surfactant was destroyed.[2]

substrate

Cubic Mesoporous

Hexagonal Mesostructured

[1]Lu *et. al.* Nature **1997**, *389*, 364.; [2]Parikh, *et. al.* Chem. Mater. **2000**, *12*, 3879.

Patterned Mesoporous/Mesostructured Films
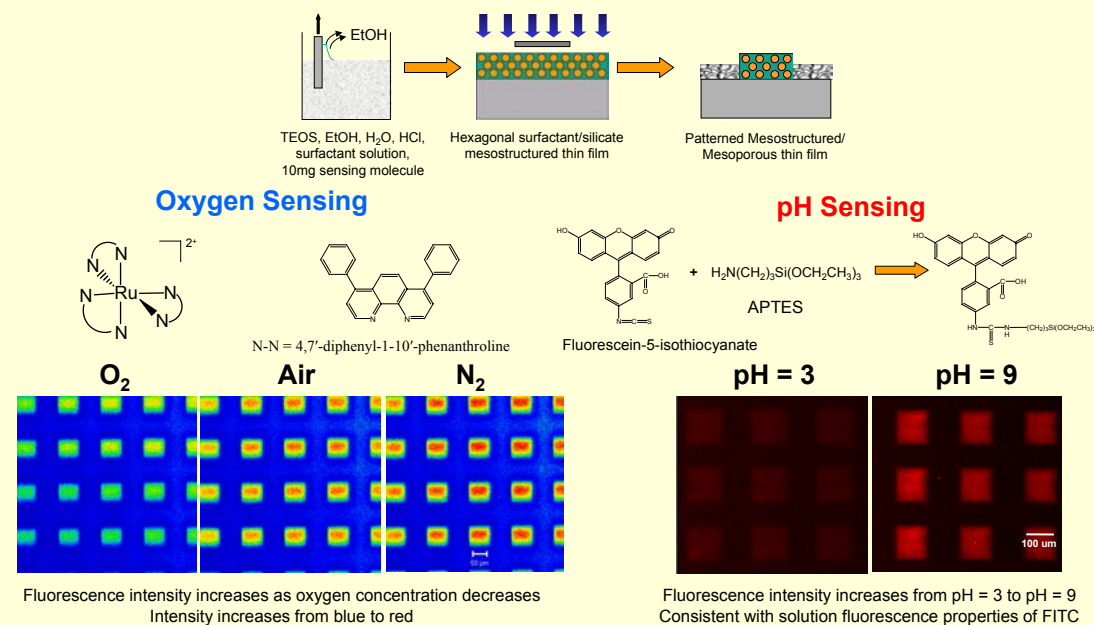
Pattern Generation and Enhancement[3]

UV-Light (185-254nm)

Optical Microscopy Mesoporous/mesostructured film

25 μ

Mesoporous

Mesostructured

0.1 m NaOH

Characterization by FTIR and Ellipsometry of Enhancement

Optical Images during NaOH immersion

t = 0 s
t = 10 s
t = 85 s
t = 3600 s

Red dot indicates region interrogated

Mesostructured region

-Log(T/T₀)

Wavenumbers (cm⁻¹)

Normalized IR Peak Intensity

Time (sec.)

mp_Si-O
ms_Si-O
ms_C-H

Mesoporous region

-Log(T/T₀)

Wavenumbers (cm⁻¹)

Normalized Thickness

Time (sec.)

mesostructured
mesoporous

[3]Dattelbaum, *et. al.* Nanoletters **2003**, in press.
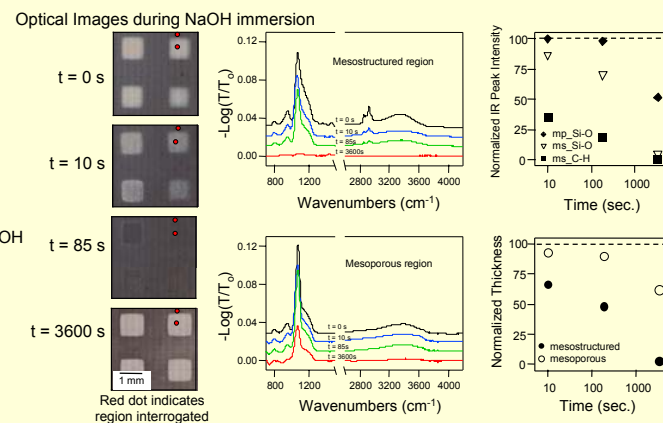
Functionalization of Patterned Nanocomposite Thin Films

TEOS, EtOH, H₂O, HCl, surfactant solution, 10mg sensing molecule

Hexagonal surfactant/silicate mesostructured thin film

Patterned Mesostructured/ Mesoporous thin film

Oxygen Sensing

N-N = 4,7'-diphenyl-1-10'-phenanthroline

pH Sensing

+ H₂N(CH₂)₃Si(OCH₂CH₃)₃

APTES

Fluorescein-5-isothiocyanate

O₂   Air   N₂

pH = 3   pH = 9

Fluorescence intensity increases as oxygen concentration decreases
Intensity increases from blue to red

Fluorescence intensity increases from pH = 3 to pH = 9
Consistent with solution fluorescence properties of FITC

Substrate-Supported Membrane Assemblies

Types of Membrane Assemblies

Self-Assembled Monolayer

Hybrid Bilayer

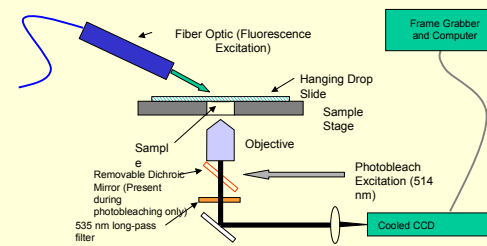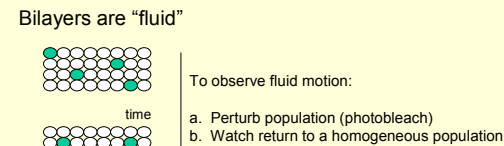Supported Bilayer

Polymer Cushioned Bilayer
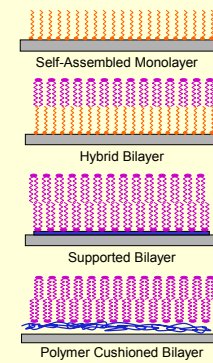
Applications Include:
· Biosensor platforms
· Prevention of biofouling
· Protein and receptor presentation
· Cell-surface interactions
· Fundamental membrane biophysics
· Membrane-protein interactions

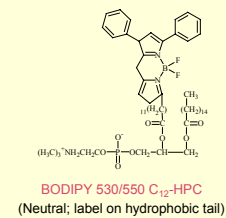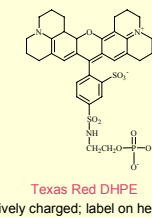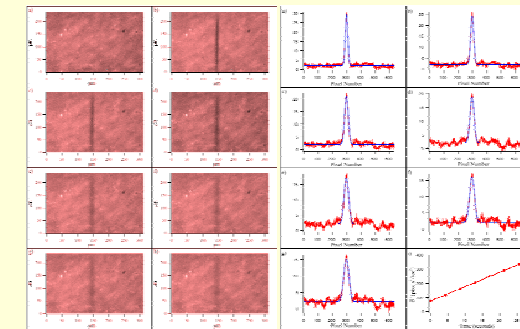Applications require control of patterning and lateral fluidity

Preparation of Membrane Assemblies

· Vesicle Fusion
  » Phospholipid vesicles (with ≤1% fluorescently labeled lipid) prepared in buffer at controlled ionic strength and pH
  » Vesicle solution contacted with substrate; Incubate ≥30 minutes
  » Exhaustively rinse with buffer
  » Store under buffer solution (indefinitely)

· Langmuir-Blodgett
  » Prepare phospholipid monolayer (with labels) at air-water interface
  » Sequential horizontal or vertical transfers at controlled π, T, sub-phase pH
  » Can prepare assemblies "wet" or "dry" and store in corresponding conditions

· Modifications
  » Polymer supports
  » Substrate choices
  » Patterning

FRAP Data for Supported Bilayer (Texas Red DHPE Label)

Fluorescence Recovery After Photobleaching (FRAP)

Bilayers are "fluid"

time

To observe fluid motion:
a. Perturb population (photobleach)
b. Watch return to a homogeneous population

Fiber Optic (Fluorescence Excitation)

Frame Grabber and Computer

Hanging Drop Slide

Sample Stage

Sample

Objective

Removable Dichroic Mirror (Present during photobleaching only)

Photobleach Excitation (514 nm)

535 nm long-pass filter

Cooled CCD

Texas Red DHPE (Negatively charged; label on head group)

BODIPY 530/550 C₁₂-HPC (Neutral; label on hydrophobic tail)

Recognition of Patterned Self-Assembled Surfaces

Masked deep-UV illumination of self-assembled monolayer

Incubate hydrophobic/hydrophilic surface with lipids to generate patterned supported/hybrid bilayer architecture

Labels in both leaflets –> 2:1 intensity contrast
Labels in outer leaflet only –> no contrast

Texas Red DHPE (negative charge)

hydrophilic
hydrophobic

Label in outer leaflet only

BODIPY 530/550 (neutral)

Label in both leaflets

Frequency

Intensity

Patterned Mesoscopic Thin Film

Supports a bilayer everywhere

Enhanced Hydrophobic/hydrophilic Character

Mesostructured thin film

Self-assemble FTS monolayer*

Pattern with UV-light

Vesicle fusion

*FTS = (Cl)₃Si(CH₂)₄(CF₂)₅CF₃

BODIPY 530/550 (0.3 mole %) in POPC lipids

Bleach

Recovery

UV-Patterned SAM

+

Sulfonated-C₆₀

Spin-cast MPS-PPV

Patterned C₆₀ Surface

MPS-PPV coated surface

C₆₀ Selectively Quenches PPV Fluorescence